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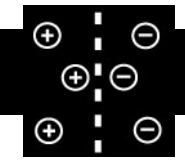
ION EXCHANGE



Catalysis: Organic Ion Exchangers

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R. L. Albright, Albright Consulting, Southampton, PA, USA

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Introduction

The ion exchange polymers most often used in catalysis are insoluble materials that can be constructed from inorganic or organic monomer units. This article will present only catalysis performed by the organic ion exchangers that are insoluble solids. There are commercial ion exchangers that are liquids, but to date they have been used very little in catalysis and, therefore, will not be included in this discussion.

Insoluble ion exchangers carry out their catalytic work in a heterogeneous rather than a homogeneous fashion and are, therefore, part of the group called heterogeneous catalysts. Heterogeneous catalysts have three very significant advantages over homogeneous catalysts: first, they are not corrosive; second, they are very readily separated from the reaction mixture by a simple filtration; and third, they are most often recyclable from one run to the next without any added treatment. Potentially, they suffer one major disadvantage over homogeneous catalysts. Intimate contact between reactants and the catalytic site is not achieved simply by mixing the heterogeneous catalyst with the reactants. In a stirred reactor, intimate contact between reactants and the homogeneous catalyst is very easily achieved and mass transport of reactants to catalyst is very rapid and almost never rate-limiting. With heterogeneous catalysis, mass transport of reactants to the catalytic site may often be the rate-limiting element, especially if the activation energy for the reaction is small and the chemical reaction is rapid. There are excellent texts and monographs on the issues surrounding heterogeneous catalysis, and the reader is referred to these for the development of a fuller understanding (see Further Reading).

Nature of Organic Ion Exchange Polymers

Chemical Composition

Organic ion exchangers are made by polymerization of organic monomers into large molecules which are made insoluble by crosslinking with a polyfunctional monomer. The nature and the level (concentration) of

the crosslinking influences the elasticity, the dimensional stability or strength of the copolymer particle, and the available space surrounding the ionogenic or catalytic site within the solvent-swelled gel phase.

Many monomers have been transformed into insoluble ion exchangers by various polyfunctional monomers, but an unabridged listing of these will not be given here. Instead, this discussion will consider only those monomer systems most used.

The most prominent insoluble copolymer matrices for constructing organic ion exchangers are those derived by the free radical copolymerization of styrene with divinylbenzene. Other matrices that have been used and are presently used to a much lesser extent are those made by the condensation polymerization of phenol (including the other hydroxylated aromatic derivatives of phenol such as catechol, resorcinol, hydroquinone, etc.) with formaldehyde and the copolymer matrices made by the free radical polymerization of the acrylate and methacrylate monomers with divinylbenzene.

The functional groups that perform the catalytic work are attached to the preformed crosslinked polymeric matrix. A vast array of chemistry allows the attachment of many different functional groups for anchoring the catalytic agent. With the aromatic polymers, electrophilic substitution reactions provide the means of functional group attachment, and with the aliphatic acrylic and methacrylic resins, the carboxyl group provides the means of functional group attachment by nucleophilic substitution reactions. A plethora of chemistry is available to build a heterogeneous catalyst upon the polymeric matrices employed to make ion exchangers.

Much of the chemistry for designing effective catalysts built upon crosslinked polymers, however, has not been pursued to a fruitful outcome. Many of the special heterogeneous catalysts have been built upon crosslinked polymers with poor mass transport in the solvent systems necessary for effective chemical transformations and, therefore, have had inferior performance to the corresponding homogeneous catalysts. This inferior performance resulting from poor mass transport has partially quenched the commercial development of what could be excellent heterogeneous catalysts when built upon the properly designed structures of the crosslinked polymers. As a result, most of the commercial effort to use ion exchangers as catalysts has been in two areas – acid- and base-catalysed reactions. Solid acids and solid bases are the two major ion exchangers employed in water demineralization and purification and have been most explored as catalysts.

The strong acid ion exchangers are sulfonated polymers of styrene crosslinked with divinylbenzene. The solid bases are copolymers of styrene and/or vinylpyridine crosslinked with divinylbenzene and functionalized to give either a quaternary ammonium hydroxide group or a tertiary amine group. Solid bases are also prepared from copolymers of the acrylate and methacrylate monomers by crosslinking with divinylbenzene followed by attachment of the amino group to the polymer via an amide linkage.

Physical Structure

The geometry of ion exchange particles as manufactured today is spherical. The bead diameters can be varied by the method of manufacture, but the standard size of commerce is a Gaussian distribution of beads ranging in diameter from 250 μm (60 mesh US Sieve Series) to about 1000 μm (18 mesh US Sieve Series). The condensation polymers of phenol with formaldehyde may still be supplied as irregularly shaped particles, but even these polymers can be made in spherical bead form, if desired. The spherical geometry arises from the method of manufacture which is by stirring a suspension polymerization of monomer droplets dispersed in an immiscible liquid. The immiscible liquid most used is water properly formulated to maintain droplet integrity throughout the transformation of monomer into polymer.

Recently a number of manufacturers of ion exchangers have developed technology for making monosized particles in which the range of size is very narrow with a uniformity coefficient of less than 1.12. Monosized particles may have an advantage in some catalytic applications if the ion exchanger being used is a gel resin. The monosized gel beads will have an advantage over a Gaussian distribution of beads if the average diffusional path length is shorter for the monosized beads than that for the Gaussian distribution. For macroporous polymers, the bead diameter has a very small impact upon the mass transport because the ingress and egress is through a continuous pore system rather than through a solvated polymer network as in a gel polymer.

Ion exchange beads have two internal polymer morphologies: one is a gel in which the network of polymer chains is continuous throughout the bead volume; the other is a macroporous structure in which the bead is constructed from small microgel particles tending towards spherical symmetry and packed together into clusters and arrays of clusters. The macroporous bead has both a continuous pore phase and a continuous gel phase, whereas the gel bead has only a continuous gel phase. Within the gel bead, there are no pores. Porosity develops only as the polymer chains are solvated by the reaction medium and become

solvent separated. Within the macroporous polymers, there are two subgroups: those with a small specific surface area ($\bar{S}$) less than about 400 to 500 $m^2\ mL^{-1}$ and those with a large specific surface area greater than about 600 $m^2\ mL^{-1}$.

The macroporous polymers with a small specific surface area have good accessibility into the core of the bead but the number of catalytic sites on the pore surface is insufficient to provide acceptable rates of catalysis. Consequently, the working phase in these beads is primarily the gel phase of the microgel. The macroporous polymers with a large specific surface area ($\bar{S}$) have sufficient catalytic sites on the internal pore surface to give acceptable rates of catalysis and are, therefore, true surface phase catalysts. **Table 1** shows these relationships for a family of sulfonated macroporous polymers.

In the macroreticular synthesis of macroporous polymers, large surface areas are achieved only by increasing the level of crosslinking in the polymerizing monomer mixture. The microgel of the resulting polymer is so tightly crosslinked that it is impenetrable even to molecules as small as methylene dichloride (CH_2Cl_2). For effective catalysis, the surface phase must be the working arena since the gel phase is impenetrable and also not functionalized. Consequently, mass transport and catalytic effectiveness are influenced quite differently within these three physical structures by the following:

1. Level of crosslinking
2. Bead diameter
3. Solvating nature towards the polymer by the reaction medium
4. Size of the reactants and/or products.

Mass Transport: A Critical Element in Performance

With ion exchangers as with other heterogeneous catalysts, mass transport of reactants into the catalytic site and mass transport of products from the catalytic site can become totally rate controlling. A qualitative tabulation of these interacting relationships is provided in **Table 2**.

For estimating the suitability or design of a macroporous polymer for effective mass transport, the equation given below, derived from the studies of Halász and Martin, has been found very useful. The appropriate pore system for good mass transport can be selected by simply knowing the molecular weight of the expected product or the largest reactant molecule.

$$d_p = 5\ d_M$$

$$d_M = 0.2457\ (MW_M)^{0.588}$$

where: d_p = pore diameter in Å of the pore system at 50% of the total pore volume of the macroporous polymer; d_M = random coil diameter in Å of either the product molecule or the largest reactant molecule; MW_M = molecular weight of product or largest reactant.

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Functional Groups – Catalytic Agents

The most studied catalytic functional group is the sulfonic acid group (–SO_3H) attached to styrene–divinylbenzene copolymers of both gel and macroporous morphologies. Many reactions catalysed by

Table 1 Intrinsic properties of a family of sulfonated porous aromatic polymers: the relationship of surface capacity, specific surface area, crosslinking density, and the working arena

Sulfonated porous polymer	*Theory weight capacity, (meq g^{-1})*	*Measured weight capacity, (meq g^{-1})*	*Rings on internal surface, (No.%)*	*Calculated theory wt. cap. on int. surface (meq g^{-1})*	*Crosslinking density (wt.%DVB)*	*Specific surface area, $\bar{S}$*		*Working phase in catalysis*
						($m^2\ g^{-1}$)	*($m^2\ mL^{-1}$)*	
Amberlyst XN-1008[a]	5.299	5.26	2.76	0.146	12	40	60	Gel phase
Amberlyst 15	5.210	5.00	3.72	0.197	20	55	82	Gel phase
Amberlyst XN-1005[b]	4.854	3.50	11.95	0.683	50	120	180	Gel phase
Amberlyst XN-1010	4.749	3.60	37.92	1.827	85	615	850	Surface phase

[a] Amberlyst XN-1008 is no longer marketed commercially. It has been replaced by Amberlyst 16 which has a similar specific surface area but is slightly more porous.
[b] Amberlyst XN-1005 is no longer commercially available.

Table 2 Qualitative relationship between polymer morphology of ion exchanger and change in reaction system

Polymer morphology	*Change in the reaction system*	*Effect on the kinetics of catalysis*
Gel polymer	Increasing level of crosslinking from 2 to 12 wt.% divinylbenzene	Decreasing rate of reaction. Gel copolymers of styrene–divinylbenzene with greater than about 6% divinylbenzene perform poorly as catalysts even in good swelling solvents
	Increasing bead diameter from 250 to 1000 μm	Decreasing rate of reaction. In good solvating reaction medium, the smaller the bead diameter, the better the catalyst performance
	Poorly solvating reaction medium for catalyst	Ineffective catalysis at any particle diameter and any crosslinking level
	Increasing size of reactants and/or products	Decreasing effectiveness as a catalyst
Macroporous polymer with small specific surface area ($\bar{S}$) ($\bar{S} < 400$–$500\ m^2\ mL^{-1}$ bead)	Increasing level of crosslinking from 6 to 25 wt.% divinylbenzene	Moderate decline in catalytic effectiveness from compensating changes. As the crosslinking level increases, the $\bar{S}$ increases and the microgel diameter decreases
	Increasing bead diameter from 250 to 1000 μm	For small to moderate sized molecules, almost no change in catalyltic effectiveness
	Poorly solvating reaction medium for catalyst	Very small impact on catalytic performance
	Increasing size of reactants and/or products	Provided the pore system is sufficient for ingress of reactants and egress of products, only a moderate decline in effectiveness
Macroporous polymer with large specific surface area ($\bar{S}$) ($\bar{S} > 600\ m^2\ mL^{-1}$ bead)	Increasing level of crosslinking from 60 to 100 wt.% divinylbenzene	Increasing catalytic effectiveness, provided pore dimensions remain large enough to accommodate entrance of reactants and exit of products. As level of DVB increases, the surface area increases
	Increasing bead diameter from 250 to 1000 μm	Little or no impact on catalytic effectiveness
	Poorly solvating reaction medium for catalyst	No impact upon catalytic effectiveness
	Increasing size of reactants and/or products	No impact upon catalytic effectiveness provided pore system allows influx of reactants and efflux of products

homogeneous strong acids have been examined for effective catalysis by strong acid ion exchangers because of their lack of corrosiveness and their ease of separation from the reaction liquor by filtration (**Table 3**). Strong acid resins with crosslinking by divinylbenzene of 8 wt.% or less work well only where the reaction medium is very polar (water, dimethylformamide, *N*-methylpyrrolidinone or dimethyl sulfoxide) and the reactants or resulting products are small (MW < 250 Da).

Strong acid macroporous polymers work well in essentially all reaction media, especially the large specific surface area, strong acid macroporous polymers where the surface phase is the catalytic arena. Here solvation of the gel phase is unimportant. The surface phase sulfonic acid groups, however, are not as powerful in protonating reactants as those buried in the gel phase – the surface sulfonic acid moiety is a weaker acid than those within the gel. By placing two sulfonic acid groups on each surface ring, by sulfonation with fuming sulfuric acid, both the acid strength and the thermal stability are increased. Sulfonated aromatic polymers with the sulfonic acid group attached directly to the aromatic ring begin to desulfonate at about 120°C, since sulfonation is acid catalysed and reversible. By attaching an electron withdrawing group, such as $-SO_2-$, $-SO_3H$, Cl, Br, F, etc., to the aromatic ring, in addition to the sulfonic acid group, the thermal stability of the strong acid resin is boosted to about 150°C.

Ion exchangers have their functional groups anchored in space relative to each other and the neighbouring groups can be used to enhance the rates of reactions of appropriately structured molecules. As an example of this effect, the rate of hydrolysis of olefinic esters is greatly enhanced by loading silver cations on to a portion of the sulfonic acid groups. At 50% loading of the cation exchanger with silver cations, the maximum rate of hydrolysis of allyl acetate is observed even though the concentration of acid

Table 3 Transformations catalysed by ion exchangers

A. Reactions catalysed effectively by strong acid resins
Acetal and ketal synthesis
Addition of carboxylic acids to olefins
Alkylation of aromatic molecules, especially activated rings such as phenols, toluene, etc.
Cumene hydroperoxide conversion to phenol and acetone
Dehydration of alcohols into olefins
Epoxidation of olefins with H_2O_2
Esterification
Etherification
Hydrolysis
Hydrolysis of starch, cellulose and saccharides
Olefin acylation
Olefin alkylation
Olefin hydration
Olefin isomerization
Olefin oligomerization
Solvolysis of epoxides
Transesterification
B. Reactions catalysed effectively by anion exchangers
Active methylene condensation reactions
Aldol condensation
Cannizzaro reaction
Cyanoethylation
Epoxide addition to carboxylic acids
Michael addition reactions
Nitrile hydrolysis to amides
C. Reactions catalysed effectively by heterogenized solid phase transition and noble metal catalysts
Epoxidation of olefins
Hydroformylation
Hydrogenation

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sites is halved. The silver ion with its propensity to complex with double bonds pulls into the resin phase a higher concentration of allyl acetate, thereby increasing the rate of hydrolysis over that of the strong acid resin without silver cations. This is a polymeric matrix effect which is not possible with a homogeneous catalyst. Polymeric matrix effects are an added advantage of solid phase over liquid phase catalysts for enhancing the catalytic effectiveness of ion exchangers.

Anion exchangers are the second most studied group of solid phase catalysts. The catalytic agents that are attached to the polymeric matrices are quaternary ammonium and tertiary amine groups. The positively charged nitrogen of the quaternary ammonium group is effective in catalysing some reactions, but most often it is the associated anion that is varied to achieve an effective catalytic agent. The positively charged nitrogen of the quaternary group is effective in catalysing epoxide addition reactions, as one example. Base catalysis is carried out with either the quaternary ammonium hydroxide or the tertiary amine group. For reactions whose products are sensitive to the base strength, a less powerful basic anion such as carbonate or acetate can be employed when the quaternary ammonium agent is the catalyst. The quaternary ammonium resin in the hydroxide form begins to decompose when used above 60°C. Other anionic forms are stable to about 150°C. The tertiary amine resins are thermally stable to about 150°C.

Phase transfer catalysis is accomplished by anion exchangers with any one of a number of appropriate nucleophilic anions associated with the quaternary ammonium group. The appropriateness of the nucleophilic anion is controlled by the nature of the chemical reaction undergoing catalysis. Phase transfer catalysts can also be designed by attaching a quaternary phosphonium group to the polymeric matrix in place of the quaternary ammonium group. Spacer arms that move the onium group further from the crosslinked polymer backbone enhance catalytic activity in phase transfer catalysis.

Crosslinked styrene–divinylbenzene copolymers have been and continue to be actively investigated as solid supports to heterogenize homogeneous catalytic agents. These solid phase catalysts have transition metals and noble metals anchored to the solid polymeric matrix through appropriate ligands. In heterogeneous form, they promote the same chemical reactions as in solution, albeit with the imposed mass transport limitations of the solid support.

See also: **II/Ion Exchange:** Historical Development; Inorganic Ion Exchangers; Novel Layered Materials: Phosphates; Novel Layered Materials: Non-Phosphates; Organic Ion Exchangers; Theory of Ion Exchange. **III/Catalyst Studies: Chromatography.**

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Historical Development

I. Grafova, Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Kiev, Ukraine

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Development of Ion Exchange Concept, Materials and Methods

The main stages in the development of ion exchange are shown in **Table 1** and **2**. Ion exchange gradually became an important separation method in water treatment, waste water purification, analytical chemistry, medicine, the food industry and many other areas of application.

The first systematic studies of ion exchange occurring in natural inorganic materials were performed during the period 1850–80, clays, sands and zeolites became objects of investigation and it was shown that soil treated with ammonium salts absorbs these ions, releasing an equivalent amount of calcium ions. Later, some natural materials found application for purification of water as well as for other purposes. At that time, the evidence for existence of ions in solution had not yet been elucidated and the concept of a double electric layer had not yet been proposed. Despite this the stoichiometry of ion exchange and its connection with aluminosilicates present in the soil were established. It was demonstrated that the degree of exchange increased up to a limiting value with the increase of concentration of salt solution, while the influence of temperature on ion exchange was shown to be less significant.

At the beginning of the twentieth century complementary investigations in the areas of synthesis and application of ion exchangers took place. Industrial production of synthetic amorphous aluminosilicate ion exchange materials was started. These materials (permutites) were used for water softening and in the treatment of sugar syrups. In the first artificial sodium aluminosilicates a substitution of sodium to calcium occurred, but the ion exchanger could be regenerated in a column by treatment with saturated sodium chloride solution.

Ion exchange materials can also be obtained by oxidation and sulfonation of coals. Some types of charcoal, soft and hard brown coals, are suitable for this purpose. They can be converted into cation exchangers after treatment with fuming sulfuric acid. As a result, sulfonic and carboxylic groups (resulting from oxidation) are introduced into the coal structure, playing the role of fixed ions. Furthermore, the coal is transformed to a gel due to polycondensation reactions. The total exchange capacity of such materials is about 1.5 meq g^{-1}.

Organic Ion Exchange Materials

Later, the ion exchange properties of some organic materials were discovered, which led to the creation

Table 1 Principal practical achievements in the field of ion exchange

Year	*Milestone*
1850–52	Discovery of ion exchange phenomenon in soil (Thompson, Way and Roy)
1903	The first synthetic inorganic ion exchanger (Harms, Rümpler, Gans)
1935	The first ion exchange resin possessing high capacity (Adams and Holmes)
1944	Development of ion exchange resin synthesis by means of copolymerization (d'Alelio)
1947	Synthesis of zeolites (Barrer)
1950	Synthesis of ion exchange membranes (Wyllie, Sollner)
1958	Synthesis of inorganic ion exchanger based on zirconium phosphate (Amphlett)
1964	Synthesis of the first crystalline zirconium phosphate of α-type structure (Clearfield and Stynes)
1975–79	Development of ion chromatography (Small, Gjerde)
1980–present	New layered materials of α- and γ-types, organic ion exchangers; improvement of ion exchange chromatography method